

Two Copper Complexes Based on Pyrazole- 3-carboxylic Acid as Heterogeneous Catalysts for Highly Selective Oxidation of Alkylbenzenes

JIANG Xiu-Yan⁽¹⁾ (蒋秀燕); RONG Nian-Xin⁽²⁾ (荣念新); QIAN Rui⁽²⁾ (钱瑞); QIU Tian-Tian⁽²⁾ (邱田田); YAO Qing-Xia⁽²⁾ (姚清侠); HUANG Xian-Qiang⁽²⁾ (黄现强)

⁽¹⁾School of Chemical Engineering, Shengli College, China University of Petroleum, Dongying 257061, China; ⁽²⁾Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry & Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, China

ABSTRACT Two new copper complexes based on pyrazole-3-carboxylic acid (H₂pca) ligand, Cu(Hpca)₂(H₂O)₂·2H₂O (**1**) and Cu₂(pca)₂(H₂O)₄ (**2**) have been synthesized and fully characterized by single-crystal X-ray diffraction (SXRD), infrared spectroscopy (IR), thermal gravity analysis (TGA), powder X-ray diffraction (PXRD) and elemental analyses. Complex **1** is mononuclear while complex **2** shows a dinuclear structure. Complex **1** crystallizes in the monoclinic system, space group *P*2₁/*c* with *Z* = 2, *a* = 6.5591(5), *b* = 21.696(2), *c* = 4.9486(2) Å, *V* = 680.94(9) Å³, *F*(000) = 366, *D*_c = 1.745 g/cm³, *μ* = 1.650 mm⁻¹, the final *R* = 0.0340 and *wR* = 0.0792. Complex **2** crystallizes in the monoclinic system, space group *P*2₁/*n* with *Z* = 2, *a* = 5.1935(4), *b* = 9.6052(7), *c* = 12.7347(9) Å, *V* = 634.44(8) Å³, *F*(000) = 420, *D*_c = 2.195 g/cm³, *μ* = 3.404 mm⁻¹, the final *R* = 0.0305 and *wR* = 0.0653. The three-dimensional frameworks of two complexes are formed by the O—H···O and N—H···O hydrogen bonding interactions. Notably, two copper complexes are further used as catalysts in the oxidation of alkylbenzenes using *t*-butylhydroperoxide (TBHP) as the oxidant and they exhibit excellent catalytic performance (Conv. up to 98.9%, Sele. up to 98.7%).

Keywords: copper complexes; crystal structure; oxidation of alkylbenzenes;

DOI: 10.14102/j.cnki.0254-5861.2011-1731

1 INTRODUCTION

In recent decades, transition-metal complexes have obtained long-lasting attention owing to their special structures and extensive applications in catalysis, adsorption, electric conducting materials, magnetic and optical materials, and so on^[1-4]. Among transition metals, copper is an important element in coordination chemistry, catalysis chemistry and a microelement necessary to life^[5-8]. Its flexible coordination modes make it easy to form mononuclear, dinuclear and multinuclear complexes^[9, 10]. Pyrazole carboxylates as a kind of multifunctional ligands play an important role in generating excellent architectures because of some advantages: firstly, the multidentate organic ligands possess potential coordination nodes and the strong coordination ability, and they exhibit diverse chelating and bridging modes; secondly, pyrazole carboxylates also act as the multiple proton donors and acceptors, and may build high-dimensional supramolecular frameworks by hydrogen-bonding or π - π stacking interactions. However, few examples are reported with the transition-metal complexes based on 1*H*-pyrazole-3-carboxylic acid owing to only one carboxyl group in the ligand^[11-13]. And it remains a significant challenge to synthesize such pyrazole-3-carboxylic acid complexes and develop their catalytic activities in some organic reactions.

Herein, we report the syntheses and structural characterizations of the mononuclear copper complex **1** and dinuclear copper complex **2**, which were obtained by the room temperature conditions or hydrothermal method. The two copper complexes have been fully characterized by SXRD, PXRD, elemental analyses, TGA and FT-IR spectroscopy. Complexes **1** and **2** were further investigated as catalysts for the oxidation of alkylbenzenes with TBHP as an oxidant.

2 EXPERIMENTAL

2.1 Instruments and reagents

All reagents and solvents were purchased from commercial sources and used without further purification. PXRD patterns of the samples were analyzed with monochromatized Cu- $K\alpha$ ($\lambda = 1.54178 \text{ \AA}$) incident radiation by a Shimadzu XRD-6000 instrument operating at 40 kV voltage and 50 mA current, and PXRD patterns were recorded from 4° to 50° (2θ) at 298 K. The C, H and N elemental analyses were conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of $4000 \sim 400 \text{ cm}^{-1}$ on a Nicolet 170 SXFT/IR spectrometer. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an Rtx-1701 Sil capillary column. TGA experiments were carried out on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10°C/min from the room temperature to 600°C under nitrogen atmosphere.

2.2 Synthesis of complex $\text{Cu}(\text{H}pca)_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (**1**)

A solution containing $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.074 g, 0.2 mmol) in 5 mL of distilled water was slowly added to a solution containing H_2pca (0.0448 g, 0.4 mmol) and NaOH (0.1 mL, 1 M in H_2O) under stirring in 5 mL of distilled water. The reaction mixture was stirred for 1 h at room temperature and filtrated. The blue block crystals of **1** were obtained by slow evaporation of the filtrate at room temperature over a period of three

weeks with the yield of 32% based on Cu. IR (KBr, cm^{-1}): 3484 (s), 3363 (s), 1660 (s), 1555 (m), 1507 (m), 1475 (m), 1382 (m), 1355 (s), 1263 (s), 1232 (w), 1133 (m), 1068 (s), 1014 (m), 942 (m), 898 (m), 839 (m), 785 (m), 649 (m), 502 (w). Anal. calcd for $\text{C}_8\text{H}_{14}\text{CuN}_4\text{O}_8$: C, 26.86; H, 3.94; N, 15.66%. Found: C, 26.91; H, 3.97; N, 15.54%.

2.3 Synthesis of complex $\text{Cu}_2(\text{pca})_2(\text{H}_2\text{O})_4$ (**2**)

A mixture of H_2pca (0.0448 g, 0.4 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.068 g, 0.4 mmol), NaOH (0.2 mL, 1 M in H_2O) and distilled water (10 mL) was sealed in a 23 mL Teflon-lined steel vessel and heated at 150 $^\circ\text{C}$ for 72 h, and then cooled to room temperature at a rate of 0.1 $^\circ\text{C}/\text{min}$. The resulting blue block crystals of **2** were obtained and washed with distilled water with a yield of 31% based on Cu. IR (KBr, cm^{-1}): 3485 (s), 1659 (s), 1557 (w), 1512 (m), 1475 (m), 1382 (s), 1356 (s), 1263 (s), 1232 (w), 1133 (m), 1068 (m), 1014 (m), 942 (m), 898 (m), 838 (m), 785 (m), 649 (w), 497 (w). Anal. calcd for $\text{C}_8\text{H}_{12}\text{Cu}_2\text{N}_4\text{O}_8$: C, 22.91; H, 2.88; N, 13.36%. Found: C, 22.98; H, 2.95; N, 13.27%.

2.4 Procedure for the catalytic oxidation of alkylbenzenes

Alkylbenzenes (0.25 mmol), copper complex (5 mol%), 70% TBHP (0.625 mmol) and benzonitrile (2 mL) were added to a 10 mL flask, and the catalytic reaction was performed at 70 $^\circ\text{C}$ for 24 h. After the reaction was completed, the resulting mixture was analyzed by GC-MS and GC.

2.5 Reuse experiments

The reuse experiments were carried out for the oxidation of diphenylmethane under the optimum conditions. After the reaction was completed, the catalyst was retrieved by filtration (5.8 mg, 96% recovery), washed with MeOH (ca. 3* 5 mL), and air-dried prior to being used for the reuse experiment. The PXRD spectrum of the retrieved catalyst was identical to that of the fresh catalyst (Fig. 6). In addition, the retrieved catalyst could be reused for the second run of oxidation of diphenylmethane. After the second run reaction was completed, the catalyst was retrieved by filtration (5.5 mg, 95% recovery), washed with MeOH (ca. 3* 5mL), and air-dried prior to being used for the third run experiment. The experiment of the third run was prepared in the same way as that for the second run, and finally the 95.7% conversion of diphenylmethane was also determined by GC. The PXRD spectrum of the third run retrieved catalyst was identical to that of the fresh catalyst (Fig. 6).

2.6 Structure determination

Single-crystal X-ray diffraction data for complexes **1** and **2** were performed with $\text{MoK}\alpha$ radiation ($\lambda =$

0.71073 Å) on a Bruker-AXS CCD diffractometer equipped with multi-scan technique at 296 K. The structures were solved by direct methods and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package^[14, 15]. The final refinements included anisotropic displacement parameters for all atoms. The selected bond lengths, bond angles and hydrogen bond parameters of **1** and **2** are shown in Tables 1 and 2, respectively.

3 RESULTS AND DISCUSSION

3.1 Structure description of $\text{Cu}(\text{Hpca})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (**1**)

The single-crystal X-ray diffraction reveals that complex **1** contains one crystallographically independent Cu^{2+} ion, one Hpca^- anion and one coordination water molecule. As shown in Fig. 1a, the Cu^{2+} ion is surrounded by two oxygen atoms, two nitrogen atoms (O(1), O(1A), N(1) and N(1A)) from two Hpca^- anions, and two oxygen atoms (O(3), O(3A)) from two coordinated water molecules, and it exhibits a distorted $\{\text{CuO}_4\text{N}_2\}$ octahedral geometry. The bond distances of the Cu–O and Cu–N are 1.9901(19)~2.508(2) and 1.976(2) Å, respectively, which are similar with those of reported copper complexes^[16]. The bond angles around Cu^{2+} ion are in the range of 81.44(8)~180.00(5)°. The Hpca^- anion adopts a chelate coordination mode: one oxygen atom and one nitrogen atom of Hpca^- anion act as coordination atoms connecting the adjacent Cu^{2+} ions, forming a five-membered ring. The adjacent mononuclear structures are connected by two kinds of hydrogen bonding interactions to form a 1D supramolecular chain, in which the first hydrogen bonding interaction is formed by the oxygen atoms (O(3)) of coordinated water molecules and the carboxylic oxygen atoms (O(1)) of Hpca^- anions with the O(3)–H(3C)··O(1) distance of 2.737(5) Å, and the second hydrogen bonding interaction is formed by oxygen atoms (O(3)) and nitrogen atoms (N(2)) of pyrazole rings from Hpca^- anions with the N(2)–H(2)··O(3) distance of 2.733(4) Å (Fig. 1b). The coordinated water molecules and carboxylic oxygen atoms (O(2)) of the adjacent supramolecular chains are linked by the O(3)–H(3D)··O(2) (2.687(0) Å) hydrogen bonding interactions to construct a 2D supramolecular layer (Fig. 1c). It is noteworthy that there are 1D water chains formed by O(4)–H(4D)··O(4) (2.814(3) Å) hydrogen bonding interactions. The existence of hydrogen-bonding interactions (O(4)–H(4C)··O(2), 2.888(7) Å) between carboxylic oxygen atoms (O(2)) of the 2D supramolecular layers and the 1D water chains which further stabilize the whole structure leads to a 3D supramolecular structure (Fig. 1d).

3.2 Crystal structure of $\text{Cu}_2(\text{pca})_2(\text{H}_2\text{O})_4$ (**2**)

The single-crystal X-ray data reveal the asymmetric unit of **2** consists of one Cu^{2+} cation, one pca^{2-} anion and two coordination water molecules (Fig. 2a). The Cu^{2+} ion is five-coordinated by one oxygen atom (O(1)) and one nitrogen atom (N(1)) from one pca^{2-} anion, one nitrogen atom (N2) from the other pca^{2-} anion and two coordination water molecules (O(3), O(4)) to give the $\{\text{CuO}_3\text{N}_2\}$ tetragonal pyramidal geometry. The bond distances of Cu–O and Cu–N are 1.9684(17)~2.3624(18) and 1.9521(19)~1.9628(19) Å, respectively. The bond angles around Cu^{2+} ion are in the range of 81.98(7)~172.52(8)°. The pca^{2-} anion adopts the monodentate-chelating coordination mode connecting Cu^{2+} ions to generate the dinuclear structure, in which two pyrazole rings from the adjacent pca^{2-} anion are parallel with a dihedral angle of 0°; and the distance of Cu...Cu is 3.9060 Å. Four pyrazole nitrogen atoms and two Cu^{2+} ions almost locate in a plane and construct a six-membered ring. The dinuclear structures are further connected to form a 1D supramolecular chain by the O–H...O hydrogen bonding interactions, which occur between the oxygen atoms (O(3)) from coordination water molecules and the carboxyl oxygen atoms (O(1)) from pca^{2-} anions with the distance of 2.720(2) Å (Fig. 2b). The final 3D supramolecular architecture is formed through O(4)–H(8)··O(3), O(3)–H(6)··O(2) and O(4)–H(7)··O(2) hydrogen bonding interactions between the neighboring 1D supramolecular chains with the distances of 2.729(2), 2.749(2) and 2.736(3) Å, respectively (Fig. 2c).

3.3 PXRD analysis

The experimental and simulated PXRD patterns of complexes **1** and **2** are shown in Fig. 3. Their peak positions were in good agreement with each other, indicating the phase purity of complexes **1** and **2**.

3.4 Thermal stability analysis

In order to study the thermal stabilities of complexes **1** and **2**, their TGA were performed. The TGA curves of complexes **1** and **2** are shown in Fig. 4. For **1**, the weight loss from room temperature to 105 °C is 19.98% (calculated 20.12%), which corresponds to the loss of lattice water and coordinated water molecules. Then the network began to decompose totally at 410 °C, and the residual is CuO. Complex **2** displayed the first weight loss of 16.69% at the temperature of 90 °C (calculated 17.17%), which was due to the departure of coordinated water molecules, and then it kept stable until 225 °C. When the temperature was above 395 °C, the framework collapsed totally.

3.5 Selective oxidation of alkylbenzenes catalyzed by complexes **1** and **2**

The oxidation of C–H bonds of alkylbenzenes, for instance, is a powerful tool to generate high value chemical feedstock from less expensive raw materials such as alkyl aromatics, and great efforts have been

made in exploring new catalysts^[17]. In this regard, the means to convert benzylic hydrocarbons into valuable compounds have received considerable attention in recent years^[18]. Herein, we report the oxidation of alkylbenzenes with TBHP as the oxidant using two copper complexes as catalysts.

To investigate the effectiveness of complexes **1** and **2** in the oxidation of alkylbenzenes, the oxidation of diphenylmethane was first examined as a standard substrate with 70% TBHP in benzonitrile at 80 °C for 24 h (Scheme 1). The conversion and selectivity of each reaction were summarized and illustrated in Fig. 5. After the preliminary optimization, we noted that complex **2** was active and more selective for the oxidation of diphenylmethane than other catalysts tested.

As the excellent performance, complex **2** was selected to examine the long-term stability in a heterogeneous system. After completion of the oxidation reaction, the catalyst can easily be separated from the reaction mixture by filtration. The recovered catalyst was re-activated by washing with methanol and further reused directly in the subsequent oxidation reactions. The experiment results displayed that after three runs no obvious loss of activity (Conv. 96.2% (1st), 96.0% (2nd), 95.7% (3rd)) was observed (Fig. 5). The PXRD spectra of **2** collected before and after the catalytic reactions indicated that the structure was maintained under turnover conditions (Fig. 6).

The mild reaction conditions, excellent stability, and high yield for the transformation of diphenylmethane to benzophenone prompted us to extend the scope of **2** as heterogeneous catalyst for other benzylic hydrocarbons. As shown in Table 3, complex **2** exhibits excellent catalytic activity for oxidation of diphenylmethane, 9H-xanthenes, fluorene and derivatives of fluorene to the corresponding aryl ketones with up to 97.6% yield (Table 3, entries 1-5). By comparison with previous reports, we found that **2** outperformed some heterogeneous catalysts, such as polyoxometalates^[19], MOFs^[20] in the oxidation of diphenylmethane, fluorene and 9H-xanthene (Table 3).

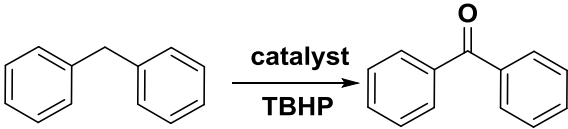
4 CONCLUSION

In summary, by controlling the reaction conditions, we have synthesized two pyrazole-3-carboxylic acid complexes **1** and **2**. The introduction of Cu²⁺ cations make **1** and **2** more stable and can be used as heterogeneous catalysts in the selective oxidation of alkylbenzenes with high catalytic activities. Specifically, complex **2** can convert alkylbenzenes to corresponding aromatic ketones efficiently and can be reused by

filtration without the loss of its activity. Investigations on the use of these complexes for other potential catalytic reactions are in progress.

REFERENCES

- (1) (a) Zhang, J. P.; Zhang, Y. B.; Lin, J. B.; Chen, X. M. Metal azolate frameworks: from crystal engineering to functional materials. *Chem. Rev.* **2012**, 112, 1001–1033; (b) Jiang, X. Y.; Rong, N. X.; Wang, G. D.; Cui, C. S.; Huang, X. Q. An imidazole-functionalized dioxovanadium complex with the highly selective oxidation of sulphides. *Chin. J. Struct. Chem.* **2017**, 36, 429–437.
- (2) (a) Yin, Y.; Tan, Z.; Hu, L.; Yu, S.; Liu, J.; Jiang, G. Isotope tracers to study the environmental fate and bioaccumulation of metal-containing engineered nanoparticles: techniques and applications. *Chem. Rev.* **2017**, 117, 4462–4487; (b) Han, C. B.; Wang, Y. L.; Liu, Q. Y. Crystal structure and magnetic properties of a dinuclear terbium compound $Tb_2(\mu_2\text{-anthc})_4(\text{anthc})_2(1,10\text{-phen})_2$. *Chin. J. Struct. Chem.* **2017**, 36, 705–710.
- (3) Paskevicius, M.; Jepsen, L. H.; Schouwink, P.; Černý, R.; Ravnsbæk, D. B.; Filinchuk, Y.; Dornheim, M.; Besenbacher, F.; Jensen, T. R. Metal borohydrides and derivatives – synthesis, structure and properties. *Chem. Soc. Rev.* **2017**, 46, 1565–1634.
- (4) Zhao, Y.; Li, Z.; Sharma, U. K.; Sharma, N.; Song, G.; Eycken, E. V. V. Copper-catalyzed alkylarylation of activated alkenes using isocyanides as the alkyl source: an efficient radical access to 3,3-dialkylated oxindoles. *Chem. Commun.* **2016**, 52, 6395–6398.
- (5) Žilić, D.; Rakvin, B.; Milić, D.; Pajić, D.; Đilović, I. Crystal structures and magnetic properties of a set of dihalo-bridged oxalamidato copper(II) dimers. *Dalton Trans.* **2014**, 43, 11877–11887.
- (6) Teong, S. P.; Yu, D.; Sum, Y. N.; Zhang, Y. Copper catalysed alkynylation of tertiary amines with CaC_2 via sp^3 C–H activation. *Green Chem.* **2016**, 18, 3499–3502.
- (7) Tirsoaga, A.; Cojocaru, B.; Teodorescu, C.; Vasiliu, F.; Grecu, M. N.; Ghica, D.; Parvulescu, V. I.; Garcia, H. C–N cross-coupling on supported copper catalysts: the effect of the support, oxidation state, base and solvent. *J. Catal.* **2016**, 341, 205–220.
- (8) Niu, M.; Li, Z.; Li, X.; Huang, X. Two chiral alkanolamine Schiff base Cu(II) complexes as potential anticancer agents: synthesis, structure, DNA/protein interactions, and cytotoxic activity. *RSC Adv.* **2016**, 6, 98171–98179.
- (9) He, J.; Yin, Y. G.; Wu, T.; Li, D.; Huang, X. C. Design and solvothermal synthesis of luminescent copper(I)-pyrazolate coordination oligomer and polymer frameworks. *Chem. Commun.* **2006**, 2845–2847.
- (10) Fernandes, T. A.; Santos, C. I. M.; André, V.; Klak, J.; Kirillova, M. V.; Kirillov, A. M. Copper(II) coordination polymers self-assembled from aminoalcohols and pyromellitic acid: highly active precatalysts for the mild water-promoted oxidation of alkanes. *Inorg. Chem.* **2016**, 55, 125–135.
- (11) Artetxe, B.; Reinoso, S.; Felices, L. S.; Vitoria, P.; Pache, A.; Martín-Caballero, J.; Gutiérrez-Zorrilla, J. M. Functionalization of kreb-type polyoxometalates with N,O-chelating ligands: a systematic study. *Inorg. Chem.* **2015**, 54, 241–245.
- (12) López-Viserasa, M. E.; Fernández, B.; Hilfiker, S.; González, C. S.; González, J. L.; Calahorra, A. J.; Colacio, E.; Rodríguez-Díez, A. In vivo potential antidiabetic activity of a novel zinc coordination compound based on 3-carboxy-pyrazole. *J. Inorg. Biochem.* **2014**, 131, 64–67.
- (13) Liu, G. N.; Zhu, W. J.; Chu, Y. N.; Li, C. C. Three d^{10} metal coordination compounds based on pyrazole-3-carboxylic acid showing mixed-ligand characteristic: syntheses, crystal structures, and photoluminescent properties. *Inorg. Chim. Acta* **2015**, 425, 28–35.
- (14) Sheldrick, G. M. *SHELXS-97, Program for X-ray Crystal Structure Solution*. University of Göttingen, Germany **1997**.
- (15) Brese, N. E.; O’Keeffe, M. Bond-valence parameters for solids. *Acta Crystallogr. Sect. B* **1991**, 47, 192–197.
- (16) Li, B.; Zhao, J. W.; Zheng, S. T.; Yang, G. Y. Hydrothermal synthesis and structure of di-copper(II)-complex substituted monovacant polyoxotungstate with a 1D chain structure. *Inorg. Chem. Commun.* **2008**, 11, 1288–1291.
- (17) Chen, H.; Deng, Y.; Yu, Z.; Zhao, H.; Yao, Q.; Zou, X.; Bäckvall, J. E.; Sun, J. 3D Open-framework vanadoborate as a highly effective heterogeneous pre-catalyst for the oxidation of alkylbenzenes. *Chem. Mater.* **2013**, 25, 5031–5036.
- (18) Shi, D.; Ren, Y.; Jiang, H.; Lu, J.; Cheng, X. A new three-dimensional metal-organic framework constructed from 9,10-anthracene dibenzoate and Cd(II) as a highly active heterogeneous catalyst for oxidation of alkylbenzenes. *Dalton Trans.* **2013**, 42, 484–491.
- (19) Yang, X. L.; Xie, M. H.; Zou, C.; He, Y.; Chen, B.; O’Keeffe, M.; Wu, C. D. Porous metalloporphyrinic frameworks constructed from metal 5,10,15,20-tetrakis(3,5-bis(carboxylphenyl))porphyrin for highly efficient and selective catalytic oxidation of alkylbenzenes. *J. Am. Chem. Soc.* **2012**, 134, 10638–10645.
- (20) He, Q. T.; Li, X. P.; Chen, L. F.; Zhang, L.; Wang, W.; Su, C. Y. Nanosized coordination cages incorporating multiple Cu(I) reactive sites: host-guest modulated catalytic activity. *ACS Catal.* **2013**, 3, 1–9.



Scheme 1. Oxidation of diphenylmethane to benzophenone with TBHP

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

Bond	Dist.	Bond	Dist.	Bond	Dist.
Complex 1					
Cu(1)–N(1) ^a	1.976(2)	Cu(1)–O(1)	1.9901(19)	Cu(1)–N(1)	1.976(2)
Cu(1)–O(1) ^a	1.9901(19)	Cu(1)–O(3)	2.508(2)	Cu(1)–O(3)	2.508(2)
Complex 2					
Cu(1)–N(2)	1.9521(19)	Cu(1)–O(3)	2.3624(18)	Cu(1)–O(1)	1.9899(17)
Cu(1)–O(4)	1.9684(17)	Cu(1)–N(1)	1.9628(19)		
Angle	(°)	Angle	(°)	Angle	(°)
Complex 1					
N(1) ^a –Cu(1)–N(1)	180.00(5)	N(1) ^a –Cu(1)–O(1) ^a	81.44(8)	O(1) ^a –Cu(1)–O(3)	90.91(7)
N(1)–Cu(1)–O(1) ^a	98.56(8)	N(1) ^a –Cu(1)–O(1)	98.56(8)	O(1)–Cu(1)–O(3)	89.09(7)
N(1)–Cu(1)–O(1)	81.44(8)	O(1) ^a –Cu(1)–O(1)	180.00(11)	N(1)–Cu(1)–O(3)	92.09(8)
N(1) ^a –Cu(1)–O(3)	87.91(8)				
Complex 2					
N(2)–Cu(1)–N(1)	98.00(8)	N(2)–Cu(1)–O(4)	92.61(8)	O(1)–Cu(1)–O(3)	88.94(7)
N(1)–Cu(1)–O(4)	168.42(8)	N(2)–Cu(1)–O(1)	172.52(8)	O(4)–Cu(1)–O(1)	86.89(7)
N(1)–Cu(1)–O(1)	81.98(7)	N(1)–Cu(1)–O(3)	92.73(7)	O(4)–Cu(1)–O(3)	90.27(7)

Symmetry code: a: $-x+1, -y+1, -z+3$

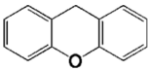
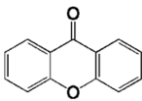
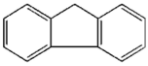
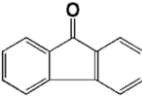
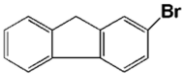
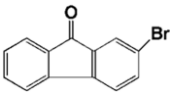
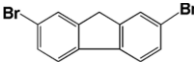
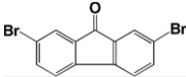
Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA
Complex 1				
N(2)–H(2)···O(3) ^a	0.860	1.970	2.733(4)	147.35
O(3)–H(3C)···O(1) ^b	0.850	1.934	2.737(5)	157.30
O(3)–H(3D)···O(2) ^c	0.850	1.884	2.687(0)	157.11
O(4)–H(4C)···O(2) ^d	0.850	2.040	2.888(7)	176.80
O(4)–H(4D)···O(4) ^e	0.850	1.965	2.814(3)	176.91
Complex 2				
O(3)–H(5)···O(1)	0.850	1.870	2.720(2)	178.99
O(3)–H(6)···O(2)	0.850	1.943	2.749(2)	157.75
O(4)–H(7)···O(2)	0.850	1.907	2.736(3)	164.76
O(4)–H(8)···O(3)	0.850	1.930	2.729(2)	156.03

Symmetry codes: a: $-x+1, -y+1, -z+2$; b: $x, y, z-1$; c: $-x, -y+1, -z+3$; d: $-x, -y+1, -z+3$; e: $x, -y+3/2, z+1/2$

Table 3. Results of Selective Oxidation of Benzylic Compounds Catalyzed by Complex 2 Using TBHP Oxidant^[a]

Entry	Substrates	Products	Conv. (%)	Sele. (%). ^[b]
1			96.2	96.5

2			97.3	98.1
3			95.7	98.5
4			98.6	98.7
5			98.9	98.3

[a] Reaction conditions: substrates (0.25 mmol), complex **2** (5 mol%), TBHP (0.625 mmol), benzonitrile (2 mL), 80 °C, 24 h.

[b] Selectivity to ketones was analyzed by GC using the naphthalene as internal standard.

The by-products are corresponding alcohols, which were analyzed by GC-MS.

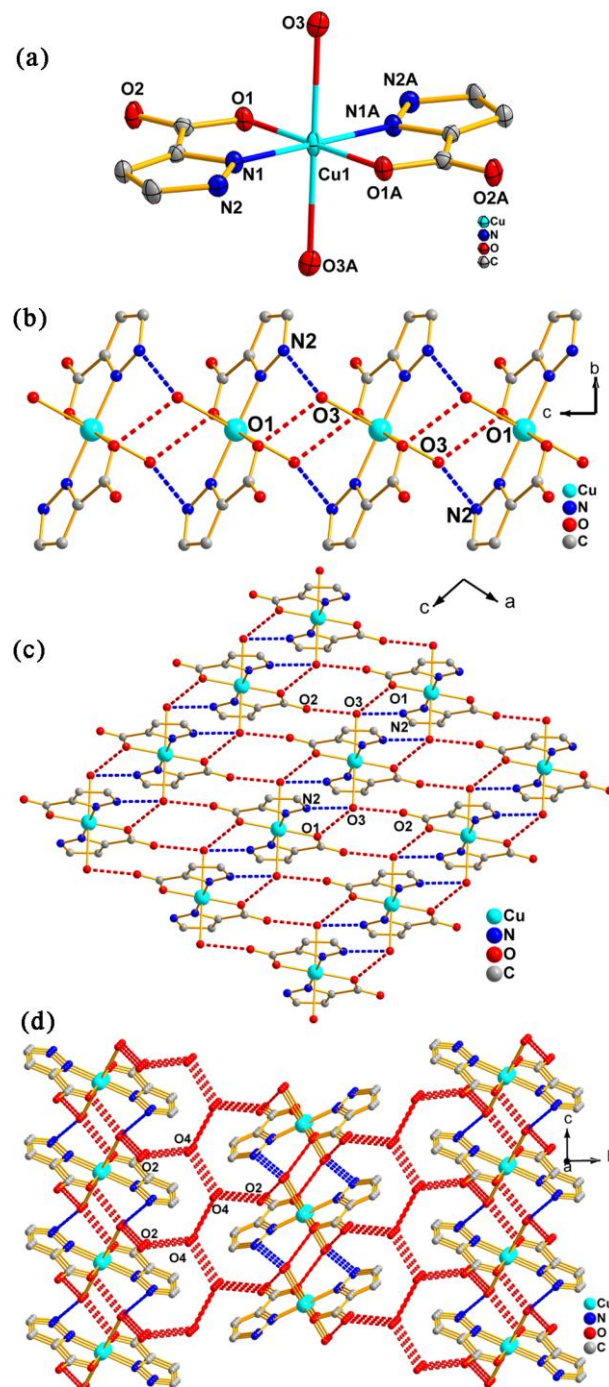


Fig. 1. (a) Coordination environment of the Cu^{2+} ions in 1 (Hydrogen atoms and lattice water molecules are omitted for clarity). (b) 1D supramolecular chain of 1 formed by hydrogen bonds in c -axis. (c) 2D supramolecular layer of 1 formed by hydrogen bonds in the ac plane. (d) 3D supramolecular framework of 1 consisting of 1D water chains

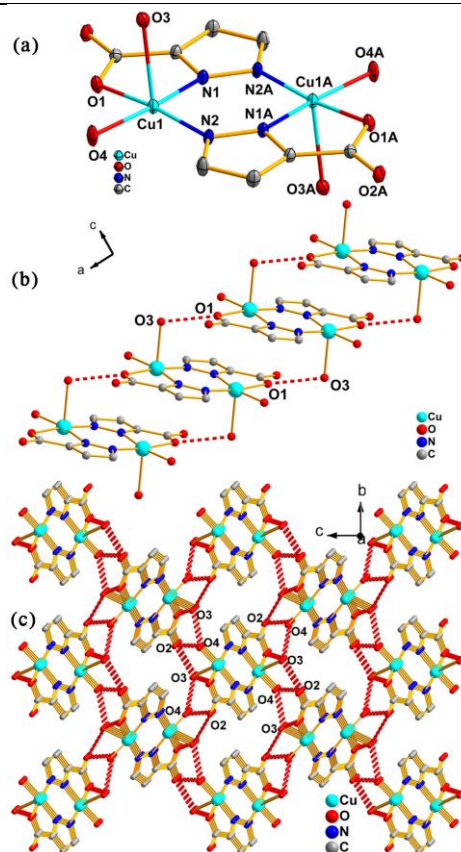


Fig. 2. (a) Coordination environment of the Cu^{2+} ions in 2 (Hydrogen atoms are omitted for clarity). (b) 1D supramolecular chain of 2 formed by hydrogen bonds in *a*-axis. (c) 3D supramolecular framework of 2 formed by hydrogen-bonding interactions

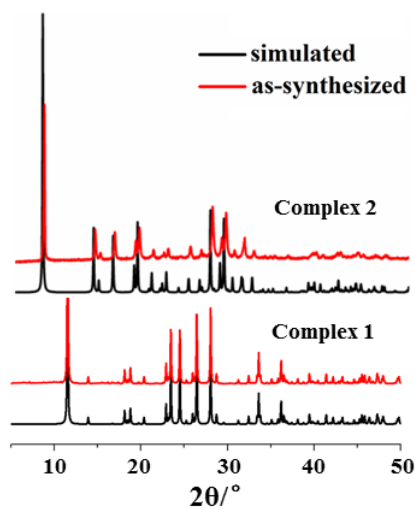


Fig. 3. Powder X-ray diffraction patterns of complexes 1 and 2

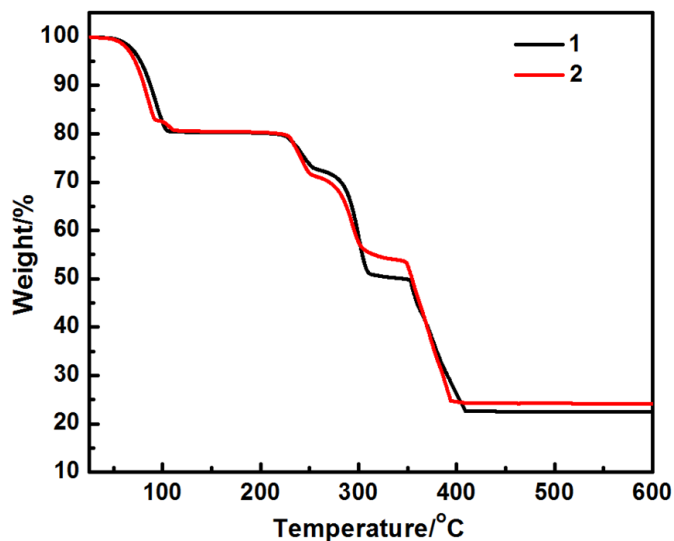


Fig. 4. TGA curves for complexes 1 and 2

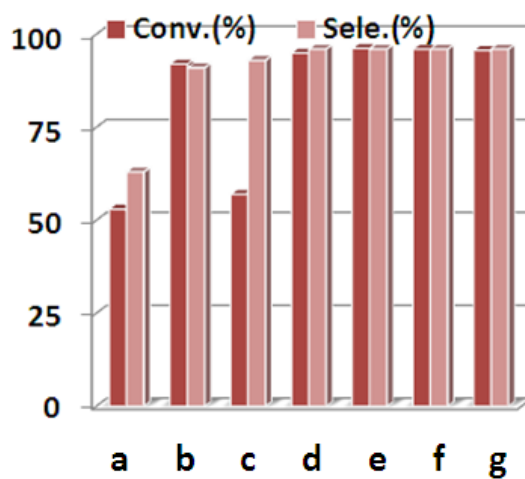


Fig. 5. Conversion of diphenylmethane to benzophenone with different catalysts. Reaction conditions: diphenylmethane (0.25 mmol), catalysts (5 mol%), 353 K, TBHP (0.625 mmol), benzonitrile (2 mL), 24 h. a) Blank; b) CuCl_2 (10 mol%); c) complex 1 (10 mol%); d) complex 2 (5 mol%); e) 1st run; f) 2nd run; g) 3rd run

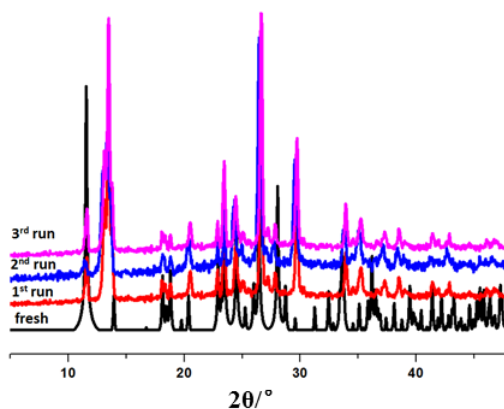


Fig. 6. PXRD spectra of complex 2 after three runs of catalytic cycles

Two Copper Complexes Based on Pyrazole-3-carboxylic Acid as Heterogeneous Catalysts for Highly Selective Oxidation of Alkylbenzenes

JIANG Xiu-Yan(蒋秀燕) RONG Nian-Xin(荣念新) QIAN Rui(钱瑞)

QIU Tian-Tian(邱田田) YAO Qing-Xia(姚清侠) HUANG Xian-Qiang(黄现强)

Two new copper complexes based on pyrazole-3-carboxylic acid ligand, $\text{Cu}(\text{Hpca})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (**1**), $\text{Cu}_2(\text{pca})_2(\text{H}_2\text{O})_4$ (**2**), have been synthesized and further studied as catalyst in the oxidation of alkylbenzenes TBHP as the oxidant. The results showed that they exhibited excellent catalytic performances (Conv. up to 98.9%, Sele. up to 98.7%).

